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THE GEORGE WASHINGTON UNIVERSITY  
Principal Investigator: Dr. N. Filipescu

SEMI-ANNUAL RESEARCH REPORT ON GRANT SC-NsG-603

Organic Systems Involving Transition Metals for Optical Laser Materials

This report will cover the period November 1, 1965 to June 30, 1966.

During this period progress has been made in the following directions:

- (1) Experimental and theoretical investigation of sensitized rare earth fluorescence in organic solvents.
- (2) Synthesis of model compounds for quantitative studies of intramolecular energy transfer between nonconjugated chromophores.
- (3) Initiate photochemical determinations to establish chemical changes occurring in rare earth chelates, sensitizers and model compounds under high intensity ultraviolet radiation.
- (4) Measurements of quantum efficiencies in homogeneous (same ligand) and mixed (two different ligands) Europium complexes. A manuscript containing these results has been accepted for publication in "Nature". A reprint copy will be attached to the next report.

(1). Sensitized Rare Earth Fluorescence in Organic Solvents

In this system an inorganic rare earth salt is dissolved in an organic solvent containing another organic compound (sensitizer). The lanthanide ion, solvent, and sensitizer (the three components) can be varied in nature and concentration such as to obtain maximum (sensitized) fluorescence conditions, the best developed systems to be tested as laser materials.

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In such systems the ultraviolet light is absorbed by the sensitizer (singlet  $\rightarrow$  singlet high intensity absorption followed by intersystem crossing to the lowest triplet state). The energy transfer step involves a collision between the sensitizer in the lowest triplet state and the rare earth ion. The process is diffusion-controlled. A large number of solvents and sensitizers have been selected after a very broad screening taking into consideration different classes of potential sensitizers and determining their spectroscopic properties, and solvents of various polarity. The lanthanide ions suitable to such a sensitization were found to be  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Dy}^{3+}$ . The influence of the following factors on the overall transfer efficiency has been studied quantitatively: viscosity, oxygen concentration, excitation wavelengths, and photokinetics. Theoretical work is in progress on the mechanism, rates of the elementary processes, competitive steps and photochemistry. Detailed results will be included probably in the next semi-annual report as manuscript.

(2) Synthesis of Model Compounds of Quantitative Studies of the Intramolecular Energy Transfer.

Significant progress has been made along the directions outlined in the previous report (November '65). A number of new chromophore-generating compounds and rigid frames have been developed which will enable us to synthesize molecular configurations in which the donor and acceptor chromophores will occupy nonconjugated rigid mutual orientations at different separation distance.

(3) Photochemical Studies

A photochemical apparatus has been set up to evaluate the chemical changes taking place in candidate laser materials, model compounds, and sensitizers under high intensity ultraviolet light.

(4) Quantum Efficiency Measurements.

The results on quantum efficiency determinations on the fluorescence of Europium homogeneous and mixed chelates have been accepted for publication in "Nature". Reprints will be attached to the next report.

(5) The "Solvent and Temperature Effects on Fluorescence Emission of Europium  $\beta$ -Diketonates" paper has been published in the Journal of Inorganic and Nuclear Chemistry. A reprint is attached to the report. The results contained in the reprint are parts of this semi-annual report.

During this period the Principal Investigator worked part time, one graduate student (Research Assistant) full time, and other two graduate students (Research Assistants) half-time.